

## MODIFIED COPOLYMER LATEX BINDER

### BACKGROUND OF THE INVENTION

#### Field of the Invention

[0001] This invention relates to a modified copolymer latex binder. More particularly, this invention relates to a modified copolymer latex binder used in the preparation of flexible nonwoven fiber mats that are useful in the roofing industry.

#### Description of the Related Art

[0002] The present invention relates generally to a copolymer latex binder used in the preparation of flexible nonwoven fiber mats, e.g., polyester fiber mats, useful in the roofing industry.

[0003] Polyester fiber mats are increasingly used in the building materials industry, as for example, in asphalt shingles, replacing sheets made of wood or cellulosic fibers. The preferred binder heretofore used in the making of polyester fiber mats has been either a vinyl-acrylic or an all acrylic emulsion, and most recently styrene-butadiene emulsions. For example, good performance properties have been obtained when a styrene-butadiene copolymer latex is used as the sole binder in the manufacture of fiber mats. However, there is a need in the roofing industry to produce polyester fiber mats that have improved hot dry elongation as measured by tensile strength not provided by a styrene-butadiene copolymer latex binder.

[0004] In accordance with the present invention, it has been found that by modifying the copolymer latex emulsion with a urea-formaldehyde resin a minimum of 15% improvement in the hot dry elongation values is achieved. This improvement is sufficient to allow an increase in production line speed by 10% or more in the formation of the flexible nonwoven fiber mats.

### SUMMARY OF THE INVENTION

[0005] Briefly, according to this invention, there is provided a modified copolymer latex binder used in the preparation of flexible nonwoven fiber mats. The modified

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copolymer latex binder comprising at least 10 wt% - 90 wt% styrene-butadiene and a corresponding amount of 90 wt% - 10 wt% of a urea-formaldehyde resin wherein the urea-formaldehyde resin is prepared by adding a short-stop agent to the urea-formaldehyde resin reaction system. The sheet includes a single layer of nonwoven or  
5 woven polyester mat coated with the modified copolymer latex binder. In an alternate embodiment, a roofing shingle, includes an asphalt-coated polyester mat embedded with granules, the polyester mat includes a plurality polyester fibers bonded with the modified copolymer latex.

[0006] The copolymer latex binder is modified with about 10% to about 90% by  
10 weight of urea-formaldehyde resin. In a preferred embodiment, the copolymer latex contains about 90% to about 10% by weight of a styrene-butadiene latex copolymer.

[0007] The flexible nonwoven fiber mats of the invention are made by applying the copolymer latex binder composition to the fiber mat, then drying and curing the binder at elevated temperatures. In a preferred embodiment, the finished fiber mat product contains  
15 about 70% to 90% by weight polyester fibers and about 10% to 30% by weight of copolymer latex binder.

[0008] In the most preferred embodiment of the invention, the copolymer latex binder is comprised of about 30% by weight of urea-formaldehyde and about 70% by weight of styrene-butadiene latex copolymer containing about 60% by weight styrene and 40% by  
20 weight butadiene.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

[0009] The following detailed description of the invention will be made with particular reference to a spun bond or dry laid process for preparing flexible nonwoven fiber mats. The process according to the invention is suitable for fibers which exclusively  
25 or predominantly, i.e. more than 50% by weight of which, contain polyolefins or polyesters, and for nonwovens which predominantly contain fibers such as these, fibers exclusively containing polyolefins or polyesters being preferred. Nonwovens of which 100% by weight consists of polyolefin or polyester fibers are particularly suitable.

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Polyolefin fibers are among the most commonly used fibers for the production of nonwovens. Examples of suitable polyolefins are polypropylene, polyethylene or copolymers of ethylene or propylene with butadiene. Polyester fibers, mainly polyethylene terephthalate fibers, are also used. Besides the fibers mentioned, other synthetic fibers suitable for the production of fiber mats useful in the roofing industry may also be used, including for example fibers of Nylon. Fibers consisting of two or more components, for example polyester/copolyester fibers or polypropylene/polyethylene fibers, are also particularly suitable. Generally, fibers having a length of about 1/4 inch to 3 inches and a diameter of about 3 to 20 microns are used.

Each bundle may contain from about 20 to 300, or more, of such fibers.

**[0010]** The dry laid process starts out from staple fibers which are normally separated by carding into individual fibers and are then laid together by an aerodynamic or hydrodynamic process to form the unbonded polyester fiber mat. The unbonded polyester fiber mat thus produced is then made up into the final fiber mat by a heat treatment

known as thermal bonding. To this end, the polyester fibers are either heated to such an extent that their surface melts and the individual fibers are joined together at their points of contact or the fibers are coated with an additive which melts during the heat treatment, thus joining the individual fibers to one another. The bonds between the individual fibers are fixed by cooling. Besides this process, any of the other processes known for bonding nonwovens fibers may of course also be used.

**[0011]** In contrast, the spunbonded process a molten melt-processable polyester material is passed through a spinneret to form a multifilamentary fibrous spinline, is drawn in order to increase tenacity, is passed through a quench zone wherein solidification occurs, is collected on a support to form a web, and is bonded to form a spun-bonded web. The drawing or attenuation of the melt-extruded spinline has been accomplished in the past by passage through a pneumatic forwarding jet or by wrapping about driven draw rolls. An apparatus arrangement utilizing both draw rolls and gas flow is disclosed in U.S. Pat. No. 5,439,364, incorporated herein by reference. The equipment utilized for spun-bonded nonwoven production in the past commonly has necessitated

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relatively high capital expenditures, multiple spinning positions, large volumes of air, and/or has presented denier variability shortcomings when one is interested in the expeditious formation of a nonwoven product on an economical basis. There is a need in the roofing industry to produce nonwoven fiber mats that have improved hot dry  
5 elongation as measured by tensile strength not previously provided by a styrene-butadiene copolymer latex.

[0012] In accordance with the present invention, it has been found that by modifying the copolymer latex emulsion binder with a urea-formaldehyde resin, a minimum of 15% improvement in the hot dry elongation values is achieved.

10 [0013] In the process according to the invention, the flexible fibers are treated with a binder containing a modified polymer latex.

[0014] In the process according to the invention, the binder is applied to the untreated nonwoven in the form of an aqueous dispersion. Any of the methods and machines typically used in the non-woven industry, for example a padding machine, may be used  
15 for this purpose. The nonwoven is first contacted with the aqueous dispersion in a bath and the nonwoven thus treated is passed between two rollers, the water being squeezed out by the pressure of the rollers. The process according to the invention is preferably designed in such a way that the fibers or nonwovens receive an add-on of finish in a quantity of 0.3 to 2.0% by weight, based on the weight of the fibers or nonwovens.

20 [0015] The process of forming fiber mats according to the invention begins with chopped bundles of fibers of a suitable length and diameter. The fibers may be sized or unsized, wet or dry, as long as they can be suitably dispersed in an aqueous dispersant medium. The bundles are added to the dispersant medium to form an aqueous slurry. Any suitable dispersant known in the art may be used. The fiber slurry then is agitated to form  
25 a workable dispersion at a suitable consistency. The dispersion then is passed to a mat-forming machine. En route to the screen, the dispersion usually is diluted with water to a lower fiber concentration.

[0016] The fibers are collected at the wire screen in the form of a wet fiber mat and the excess water is removed by vacuum in the usual manner. The wet mat now is ready

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for application of the binder composition thereto, which is accomplished by soaking the mat in an excess of binder solution and dewatered to remove excess binder solution. The mat then is dried and the binder composition is cured in an oven at elevated temperatures, generally at least at about 400 degree Fahrenheit. This heat treatment alone will effect curing; alternatively, but less desirable, catalytic curing may be used, such as with an acid catalyst, e.g. ammonium chloride or p-toluene sulfonic acid.

[0017] The modified copolymer latex binder composition of the invention is prepared by blending a urea-formaldehyde resin with a copolymer latex. Suitably, the binder composition comprises about 10% to 90% by weight of the urea-formaldehyde resin and a corresponding amount of about 90% to 10% by weight of the latex copolymer. Preferably, it consists of about 30% by weight of the urea-formaldehyde and about 70% by weight of the latex copolymer.

[0018] The latex copolymer may be a styrene-butadiene copolymer latex, styrene-acrylic copolymer latex, acrylic copolymer latex, vinyl-acrylic copolymer latex, or an ethylene-vinyl acetate copolymer latex. In a most preferred embodiment, the copolymer latex is a styrene-butadiene copolymer latex.

[0019] The latex copolymer may be formed by aqueous emulsion polymerization of one or more acrylic ester monomers including methyl acrylate, ethyl acrylate,, 2-ethyl hexyl acrylate, methyl methacrylate, butyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate and hydroxypropyl methacrylate; acrylamide or substituted acrylamides, styrene or substituted styrenes; butadiene; vinyl acetate or other vinyl esters; acrylonitrile or methacrylonitrile, carboxylic acid monomers, for example, acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid, 2-methyl maleic acid, itaconic acid, and salts thereof. Alternatively, ethylenically unsaturated anhydrides which form carboxylic acids during polymerization may be used such as, for example, maleic anhydride itaconic anhydride, acrylic anhydride and methacrylic anhydride.

[0020] In the most preferred embodiment, the styrene-butadiene latex copolymer component of the binder composition suitably may contain about 10% to about 90% by weight of styrene and a corresponding amount of about 90% to about 10% by weight of

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butadiene, modified by a cross-linking agent such as N-methylol acrylamide and the like. Small amounts of other monomers, such as carboxylic acids, e.g. methacrylic, fumaric or itaconic acid, also may be present, if desired, in the styrene-butadiene copolymer. In the most preferred embodiment, about 30% to 70% by weight styrene and 70% to 30% by weight butadiene is used; optimally the ratio is about 40% by weight styrene to about 60% by weight butadiene.

[0021] The latex copolymer is normally prepared by free radical emulsion polymerization. The charge compositions used in the preparation of such latices contain the monomers, at least one surfactant, and at least one free radical initiator. The above monomers are polymerized in the presence of water, free radical initiators, anionic surfactants, and chelating agents to form the latex binder of the present invention using conventional emulsion polymerization procedures and techniques except as otherwise provided herein.

[0022] The free radical initiators utilized to polymerize the monomers of the present invention include sodium persulfate, ammonium persulfate, potassium persulfate and the like. Other free radical initiators can be utilized which decompose or become active at the polymerization temperature such as various peroxides, e.g., cumene hydroperoxide, dibenzoyl peroxide, diacetyl peroxide, dodecanoyl peroxide, di-t-butyl peroxide, dilauroyl peroxide, bis(p-methoxy benzoyl) peroxide, t-butyl peroxy pivalate, dicumyl peroxide, isopropyl percarbonate, di-sec-butyl peroxidicarbonate, various azo initiators such as azobisdimethyvaleronitrile, 2, 2'-azobisisobutyronitrile, 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis-2-methyl-butyronitrile, 2,2'-azobis(methylisobutyrate), and the like and mixtures thereof. The amount of the free radical initiator is generally from about 0.1 to 2, and preferably from about 0.5 to 1.0 parts by weight per 100 parts by weight of the total amount of monomers added.

[0023] Optional chain transfer agents include mercaptans such as the alkyl and/or aryl(alkyl) mercaptans having from about 8 to about 18 carbon atoms and preferably from about 12 to about 14 carbon atoms. The tertiary alkyl mercaptans having from about 12 to about 14 carbon atoms are highly preferred. Examples of specific chain transfer agents

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include n-octyl mercaptan, n-dodecyl mercaptan, t-octyl mercaptan, t-dodecyl mercaptan, tridecyl mercaptan, tetradecyl mercaptan, hexadecyl mercaptan and the like, as well as mixtures thereof. The amount of the chain transfer agent utilized is from about 0.2 to 2.5, and preferably from about 0.5 to 1.5 parts by weight per 100 parts by weight of the total amount of monomers added.

[0024] The surfactants include sodium dodecylsulfate, sodium dodecylbenzene sulfate, sodium dodecyl-naphthalene sulfate, dialkylbenzenealkyl, sulfates, sulfonates and the like, especially preferred is the dihexyl ester of sodium sulfosuccinate. The amount of surfactant present is sufficient to obtain an aqueous emulsion of the monomers. Such an amount is typically from about 0.5 to 1.5 parts by weight per 100 parts by weight of the total amount of monomers added.

[0025] Chelating agents may also be used during polymerization to tie up various metal impurities as well as to achieve a uniform polymerization. Examples of specific chelating agents include ethylene diamine tetra-acetic acid, nitrilotriacetic acid, citric acid, and their ammonium, potassium and sodium salts. The amounts of the chelating agents may range from about 0.01 to 0.2 parts by weight per 100 parts by weight of the total amount of monomers added.

[0026] The urea-formaldehyde resins of the binder composition is a urea-formaldehyde resin prepared by termination by adding a short-stop agent of a type well known in the art to the reaction system after a predetermined period of time. The polymerization of the urea-formaldehyde resin is terminated by adding the short-stop agent to the reaction system after a predetermined period of time. The resultant polymer is stabilized by removing its unstable terminal portion by hydrolysis or by blocking the unstable terminal portion by an esterification method, etc. A stabilizer, etc., may be further added to the stabilized copolymer as required before practical use. The urea-formaldehyde resin is commercially available, from Dynea Oy of Helsinki, Finland. In a preferred embodiment, the urea-formaldehyde resin is sold under the designation "2023-30" by Dynea Oy of Helsinki, Finland.

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[0027] The resin and latex copolymer components of the binder composition are quite compatible. Accordingly, they are intimately admixed in aqueous solution to form a stable emulsion which does not become gummy, or gel, even after prolonged storage, e.g. for periods of a week or longer, which is advantageous in practical commercial use of the composition.

[0028] It has been found that the modified latex copolymer is unstable unless the pH of the latex is adjusted to between 7.0 - 8.0 by a non-volatile alkaline agent such as sodium hydroxide and the like. In a preferred embodiment, the non-volatile alkaline agent is triethanolamine. If the pH of the latex is adjusted with a volatile agent such as ammonia the resultant polymer will tend to set up after only a few days whereas if the pH is adjusted with a non-volatile alkaline agent the latex is usually stable for three months or more at ambient temperature with no apparent increase in viscosity.

[0029] The modified latex binder composition can be used on spun bond and air-laid nonwoven polyester substrates. In a preferred embodiment, the fiber mats are used as at least one of the substrates in the manufacture of a roofing shingle. Shingles generally have been made with a substrate of either organic fiber saturated with asphalt or chopped polyester fiber with a urea-formaldehyde binder. Typically, the substrate is first coated with a mixture of asphalt and fillers such as limestone, sand or stone dust. The coated substrate then is covered with colored granules to give aesthetic appeal to the front of the shingles.

[0030] A first substrate includes a foundational lamina comprising a polyester mat to give the overall product form and strength. A second substrate which, typically, comprises an asphalt material, overlies, and is adhered to, the first substrate. Finally, a third substrate overlies, and is adhered to the second substrate. The third substrate comprises a treated weather surface which not only serves a protective function, but also makes the shingle aesthetically pleasing.

[0031] In a first step of the manufacturing process of a roofing shingle, a continuous sheet of polyester mat substrate is paid out from a roll. The polyester mat substrate can be any type known for use in reinforcing asphalt-based roofing materials, such as a web,



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scrim or felt of polyester fibers. Combinations of materials can also be used in the substrate.

[0032] The sheet of substrate is passed from the roll through an accumulator. The accumulator allows time for splicing one roll of substrate to another, during which time  
5 substrate within the accumulator is fed to the manufacturing process so that the splicing does not interrupt manufacturing.

[0033] Next, the polyester mat is passed through a coater where an asphalt coating is applied to the polyester mat. The asphalt coating can be applied in any suitable manner. In the illustrated embodiment, the polyester mat is submerged in a supply of hot, melted  
10 asphalt coating to completely cover the polyester mat with the tacky coating. However, in other embodiments, the asphalt coating could be sprayed on, rolled on, or applied to the polyester mat by other means.

[0034] The term "asphalt coating" means any type of bituminous material suitable for use on a roofing material, such as asphalts, tars, pitches, or mixtures thereof. The asphalt  
15 can be either a manufactured asphalt produced by refining petroleum or a naturally occurring asphalt. The asphalt coating can include various additives and/or modifiers, such as inorganic fillers or mineral stabilizers, organic materials such as polymers, recycled streams, or ground tire rubber. Preferably, the asphalt coating comprises asphalt and inorganic fillers or mineral stabilizers.

20 [0035] The asphalt-coated polyester mat is then passed beneath a granule dispenser for the application of granules to the upper surface of the asphalt coating. After deposit of the granules, the sheet is turned around a slate drum to press the granules into the asphalt coating and to temporarily invert the polyester mat.

[0036] Preferably, the continuous roofing shingle can be cut cleanly and easily during  
25 the roofing material manufacturing process, such as when the sheet of roofing material is cut into shingles and when the tabs are cut in a shingle. The clean cutting means that no strings or other portions of the web material are seen protruding from the edges of the cut roofing material.

[0037] It should be noted that the web can be manufactured separately before the shingle manufacturing process, or it can be manufactured simultaneously with manufacturing the shingle. The continuous sheet of asphalt-based roofing material is then cut by a cutting apparatus of a type well known in the art into individual shingles, into  
 5 pieces to make laminated shingles, or into suitable lengths for commercial roofing or roll roofing. The roofing material is then collected and packaged.

[0038] The following examples are intended to illustrate the method for treating a flexible non-woven substrate to which this invention is directed. They are not intended to limit the invention as other applications of the invention will be obvious to those of  
 10 ordinary skill in the art.

#### Example 1

[0039] Preparation of aqueous admixture of Styrene Butadiene (SB) emulsion polymers with Urea-Formaldehyde (UF) resins. The SB latices used in this preparation  
 15 are those manufactured by Omnova Solutions Inc., and include polymers containing self-crosslinking and/or hydroxy containing monomers.

[0040] The UF resin used in this preparation is identified as resin 2023-30 and is manufactured by Dynea Corp. (formerly Neste Resins).

[0041] Various blends of Styrene/Butadiene latices with UF resin, ranging from 90:10 to 50:50 were prepared but the preferred ratio is 70 parts latex to 30 parts resin based on  
 20 dry weight. More than 50 parts of <sup>UF</sup> resin can result in coagulation of the blend.

[0042] Other additives may be added to this blend such as scavenger to reduce formaldehyde emission, anti-oxidant to prevent premature oxidation.

[0043] The pH of the blend is adjusted to 7.0-7.5 with a non-volatile alkaline agent, such as sodium hydroxide. Specially effective as alkaline agent are alkyl amines such as  
 25 triethanolamine (TEA) or dimethylethanolamine (DMEA).

[0044] The preferred emulsion, designated in Table 1 as Emulsion 1, had a composition of 70 parts dry styrene/butadiene emulsion and 30 parts dry U/F resin and

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had solid content of 45%, viscosity of less than 250 cps and a pH of 7.5 adjusted with TEA. Stability on some of these emulsions are shown in Table 1.

[0045] In testing the binders prepared in this invention, a polyester spunbonded, needle punched mat was saturated in a low solids (17%) emulsion bath. Excess emulsion was removed by passing the saturated mat through nip rolls to give samples containing 23% binder on the weight of the polyester. The saturated mat was cured in a forced air oven for 3.5 minutes at a temperature of 215 degrees C. Strips were then cut 1" by 6" in both machine direction and cross direction. Tensile values were measured on an Instron tensile tester Model 5565 equipped with an environmental chamber at crosshead speed of 100 Mm/min. The gage length at the start of each test was 4 inches.

[0046] For tear testing, strips were cut 2 inches by 4 inches along both machine and cross directions and tested using the same Instron as above.

[0047] In order to evaluate the high temperature resistance of the binder, the % strain at 180 degrees C were determined at 5 Kg - 18 Kg load using strips cut 2 inches by 7 inches along machine direction only. The % strain measures dimensional changes in a sample as a function of temperature. Lower dimensional changes in the sample represent higher temperature resistance - i.e. lower % strain values are better. Tensile, tear and % strain values are shown in Table 2 for a number of emulsions.

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Table 1

Emulsion 1	pH adjusted with	Stability Room Temp.	Stability at 35 Degrees C
With Dynea UF resin	TEA ammonia	3 months 14 days	1 month 7 days
With other UF resin	TEA ammonia	30 days 14 days	14 days 14 days

[0048] Stability is measured by viscosity change, pH change and absence of coagulum. Three month stability means that the emulsion has not change in viscosity, pH may or may not have changed by much and the polymer is free of coagulum.

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Table 2

Latex/UF ratio	Emulsion 1	Emulsion 2	Emulsion 3	Emulsion 4
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	70/30	60/40	50/50	Latex only
Tensile MD	31.80	32.52	34.10	32.67
Tensile CD	24.36	25.06	25.91	24.61
Tear MD	7.89	7.32	6.91	7.95
Tear CD	4.29	4.00	3.67	4.34
% Strain				
5 Kg	2.65	2.77	2.98	5.38
8 Kg	3.55	3.68	3.45	12.37
10 Kg	7.62	7.54	7.30	16.92
12 Kg	11.73	11.21	11.10	22.30
14 Kg	14.90	14.77	14.65	29.98
16 Kg	18.75	18.44	18.10	41.80
18 Kg	22.06	21.66	21.35	56.31

[0049] As the above results show, superior high temperature resistance properties can be obtained utilizing the styrene-butadiene UF emulsion described herein. This property is very desirable as it allows for faster conversion speed and less neck-down at the asphalt saturation plant.

[0050] The documents, patents and patent applications referred to herein are hereby incorporated by reference.

[0051] While the invention has been specifically described in connection with certain specific embodiments thereof, it is to be understood that this is by way of illustration and not of limitation, and the scope of the appended claims should be construed as broadly as the prior art will permit.